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Division of Materials Chemistry - Polymer Controlled Synthesis -

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Gwangju Institute of Science and Technology, Korea, 31 January 2008
University of Leicester, UK, 11 March 2008
Queen's University, Canada, 20 May 2008
The University of Tokyo, Japan, 16–17 September 2008
Technical University of Denmark, Denmark, 10 November 2008
Pohang University of Science and Technology, Korea, 10 November 2008
Nanyang Technological University, Singapore, 11 December 2008

Scope of Research

Our research program focuses on development of new synthetic methods, which enable precise control of polymers in terms of their size and structure. Our attention is especially directed to control of reactive carbon species, such as carbon centered radicals and carbocations, with the aid of synthetic organic chemistry, element chemistry, computational chemistry, and so on. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

Research Activities (Year 2008)

Publications

Kayahara E, Yamago S, Kwak Y, Goto A, Fukuda T: Optimization of Organotellurium Transfer Agents for Highly Controlled Living Radical Polymerization, *Macromolecules*, **41**, 527-529 (2008).

Yamada T, Mishima E, Ueki K, Yamago S: Phenyltellanyl Triflate (PhTeOTf) as a Powerful Tellurophilic Activator in the Friedel-Crafts Reaction, *Chem. Lett.*, 650-651 (2008).

Yamago S, Matsumoto A: Arylthiols as Highly Chemo-selective and Environmentally Benign Radical Reducing Agents, *J. Org. Chem.*, **73**, 7300-7304 (2008).

Yamago S, Yamada T, Togai M, Ukai Y, Kayahara E, Pan N: Synthesis of Structurally Well-Defined Telechelic

Polymers by Organostibine-Mediated Living Radical Polymerization. *In Situ* Generation of Functionalized Transfer Agents and Selective ω -End Group Transformations, *Chem. Eur. J.* (in press).

Presentations

“A New Thiobismuthine Cocatalyst in Organobismuthine-Mediated Living Radical Polymerization”, Yamago S, Kayahara E, American Chemical Society National Meeting, 5th Controlled/Living Radical Polymerization Symposium, Philadelphia, USA, 17–21 August 2008 (invited).

“Reinforcing Effect of Strain-Induced Crystallization in Natural Rubber”, Tosaka M, The 144th Symposium on Rubber Technology, Tokyo, Japan, 20 August 2008 (invited).

Synthesis of Structurally Well-Defined Telechelic Polymers by Organobismuthine-Mediated Living Radical Polymerization

There has been growing interest in new synthetic methods for the preparation of well-defined polymers with controlled chain-end functional groups. These end-functional polymers, as exemplified by telechelic polymers, serve as precursors not only for block and graft copolymers, but also for cyclic, branched, and cross-linked polymers. We have recently reported organostibine compounds mediate living radical polymerization with varieties of vinyl

monomers. While introduction of functionality into the chain transfer agents would enhance the abilities for the synthesis of telechelic polymers, strong basic conditions required for preparation of the transfer agents have limited this possibility. We report here a new synthetic route to organostibine chain transfer agents from diazo-initiators and distibines. As the synthesis proceeds under neutral conditions, a variety of polar functional groups can be introduced into the chain transfer agent and, thus, the α -polymer ends. Subsequent transformation of the organostibine ω -polymer ends provides structurally well-defined telechelic polymers.

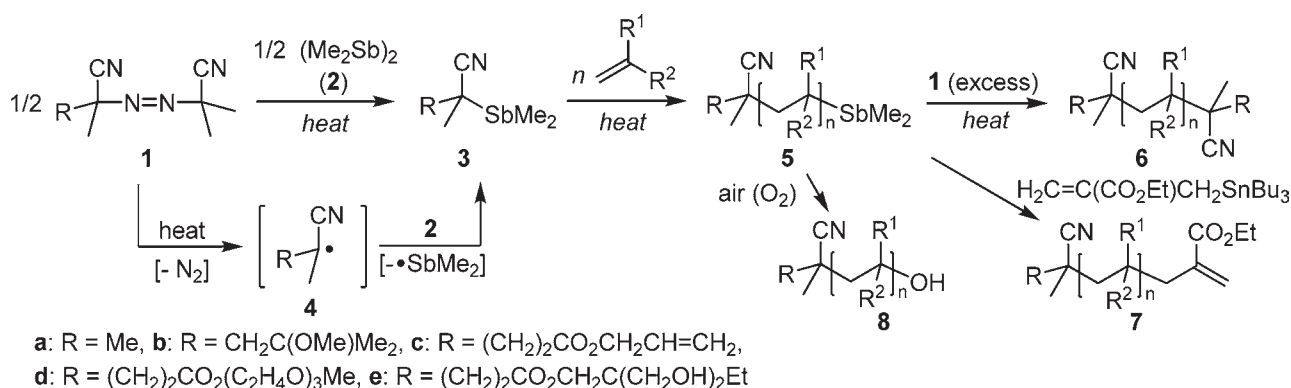


Figure 1. Synthesis of telechelic polymers by organostibine-mediated living radical polymerization.

“Synthesis of Structurally Well-Defined Telechelic Polymers by Organostibine-Mediated Living Radical Polymerization. *In Situ* Generation of Functionalized Chain Transfer Agents and Selective End Group Transformations”, Yamago S, 18th International Symposium on Fine Chemistry and Functional Polymers & IUPAC 4th International Symposium on Novel Materials and Synthesis, Zhenjiang, China, 15–18 October 2008 (invited).

“Synthesis of Structurally Well-Defined Telechelic Polymers by Organostibine-Mediated Living Radical Polymerization”, Yamago S, The 2nd Japan-Korea Joint Seminar 2008 and International Symposium. Synthetic Application of Advanced Functional Materials, Tokyo, Japan, 6–7 November 2008 (invited).

“Taming Radical Species. Development of Living Radical Polymerization Mediated by Heavier Organoheteroatom Compounds”, Yamago S, The 4th RIKEN Symposium on Frontier of Organometallic Chemistry, Wako, Japan, 14 November 2008 (invited).

“Organotellurium Mediated Living Radical Polymerization Initiated by Direct C-Te Bond Photolysis”, Yamago S, International Symposium on Advanced Green Catalysis and Materials, Taipei, Taiwan, 18–19 November 2008 (invited).

“Synthesis of Structurally Well-Defined Telechelic Polymers by Organostibine-Mediated Living Radical Polymerization”, Yamago S, Post-ISOR Symposium, Taipei, Taiwan, 24 November 2008 (invited).

Grants

Yamago S, Precise Control of Radical Reactions Using Synergetic Effects of “Heavy” Heteroatom Compounds, Grant-in Aid on Priority Areas, 1 October 2006–31 March 2010.

Yamago S, Torey Science Foundation, Torey Science and Technology Grant, 1 April 2008–31 March 2010.

Yamago S, Nagase Science and Technology Foundation Grant, 1 April 2008–31 March 2009.

Tsuji M, Structure Analysis of Poly(dioxanone) Nanofibers Prepared by Electro-Spinning Method, Grant-in Aid for Scientific Research, (C), 1 April 2007–31 March 2009.

Tosaka M, Near-Field Optical Effects of Self-Assembled Nanoparticle Chains on Oriented Polymer Layers, The Ogasawara Foundation for the Promotion of Science & Engineering Grant, 1 April 2007–31 March 2008.

Tosaka M, Formation of Nanoparticle Arrays Using Alignment of Polymer Molecules, Grant-in Aid for Scientific Research, (C), 1 April 2008–31 March 2011.